

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 05-01-2015		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-Aug-2009 - 14-Aug-2014	
4. TITLE AND SUBTITLE Final Report: Understanding and Quantifying the Reactivity of Energetic NanoParticles and NanoComposites			5a. CONTRACT NUMBER W911NF-09-1-0214		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Michael Zachariah			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Maryland - College Park 3112 Lee Building College Park, MD 20742 -5141			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 55832-EG.36		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT					
15. SUBJECT TERMS nanoenergetics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			Michael Zachariah
					19b. TELEPHONE NUMBER 301-405-4311

Report Title

Final Report: Understanding and Quantifying the Reactivity of Energetic NanoParticles and NanoComposites

ABSTRACT

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
03/22/2011 3.00	X. Ma and M.R. Zachariah. "Oxidation Anisotropy and Size Dependent Reaction Kinetics of Zinc Nanocrystals" , Journal of Physical Chemistry C, (06 2009): . doi:
03/22/2011 11.00	S. Chowdhury, K. Sullivan, N. Piekiet, L. Zhou and M. R. Zachariah. "Diffusive vs. Explosive Reaction at the Nanoscale" , Journal of Physical Chemistry C, (10 2009): . doi:
03/22/2011 10.00	K. Sullivan, W-C Chiou, R. Fiore and M.R. Zachariah. In-situ microscopy of rapidly heated nano-Al and nano-composite thermites , Applied Physics Letters, (08 2010): . doi:
03/22/2011 9.00	L. Zhou, N. Piekiet, S. Chowdhury, M.R. Zachariah, . "Time Resolved Mass Spectrometry of the Exothermic Reaction between Nanoaluminum and Metal Oxides: The Role of Oxygen Release" , Journal of Physical Chemistry C, (04 2010): . doi:
03/22/2011 8.00	K. Sullivan and M.R. Zachariah. Simultaneous Pressure and Optical Measurements of Nanoaluminum Thermites: Investigating the Reaction Mechanism , Journal of Propulsion and Power, (06 2010): . doi:
03/22/2011 7.00	B. Henz, T. Hawa, and M.R. Zachariah. "On the Role of Built-in Electric Fields on the Ignition of Oxide Coated NanoAluminum: Ion mobility versus Fickian Diffusion." , Journal of Applied Physics, (01 2010): . doi:
03/22/2011 6.00	B. Henz, T. Hawa, and M.R. Zachariah. "Molecular Dynamics Simulation of the Kinetic Reaction between Ni and Al Nanoparticles" , Journal of Applied Physics, (06 2009): . doi:
03/22/2011 5.00	G. Young, N. Piekiet, S. Chowdhury, and M. R. Zachariah. "Ignition Behavior of a-Alane" , Combustion Science and Technology, (12 2009): . doi:
03/22/2011 4.00	L. Zhou, N. Piekiet, S. Chowdhury, D. Lee and M. R. Zachariah. "Transient ion ejection during nanocomposite thermite reactions" , Journal of Applied Physics, (10 2009): . doi:
09/26/2011 12.00	N. Piekiet,, S. Chowdhury, , M.R. Zachariah,, L. Zhou,. Time Resolved Mass Spectrometry of the Exothermic Reaction between Nanoaluminum and Metal Oxides: The Role of Oxygen Release", Journal of Physical Chemistry C, (12 2010): 14269. doi:

- 09/26/2011 13.00 Richard E. Cavicchi, Michael R. Zachariah, Nicholas W. Piekiet. Rapid-heating of energetic materials using a micro-differential scanning calorimeter, *Thermochimica Acta*, (7 2011): 0. doi: 10.1016/j.tca.2011.04.015
- 09/26/2011 15.00 K.T. Sullivan, N.W. Piekiet, C. Wu, S. Chowdhury, S.T. Kelly, T.C. Hufnagel, K. Fezzaa, M.R. Zachariah. Reactive sintering: An important component in the combustion of nanocomposite thermites, *Combustion and Flame*, (9 2011): 0. doi: 10.1016/j.combustflame.2011.07.015
- 10/01/2012 16.00 K. T. Sullivan, N. W. Piekiet, S. Chowdhury, C. Wu, C.E. Johnson, M. R. Zachariah. Ignition and Combustion Characteristics of Nanoscale Al/AgIO₃: A Potential Energetic Biocidal System, *Combustion Science and Technology*, (01 2011): 285. doi:
- 10/01/2012 25.00 D. A. Firmansyah,, K. Sullivan, , K-S. Lee,, Y. H. Kim, , R. Zahaf, , M. R. Zachariah, D. Lee . Microstructural Behavior of the Alumina Shell and Aluminum CoreBefore and After Melting of Aluminum Nanoparticles, *J Phys Chem* , (01 2012): 404. doi:
- 10/01/2012 18.00 N. Piekiet, M.R. Zachariah. N.W. Piekiet and M.R. ZachariahDecomposition of Aminotetrazole Based Energetic Materials under High Heating Rate Conditions, *J Phys Chem A*, (10 2012): 1519. doi:
- 10/01/2012 17.00 K. Sullivan,, S. Chowdhury, , C. Wu, , G. Jian,, L. Zhou, M. R. Zachariah . Encapsulation of Perchlorate Salts within Metal Oxides for Application as Nano-Energetic Oxidizers, *Advanced Functional Materials*, , (10 2012): 78. doi:
- 11/25/2013 26.00 Guoqiang Jian, Lu Liu, Michael R. Zachariah. Facile Aerosol Route to Hollow CuO Spheres and its Superior Performance as an Oxidizer in Nanoenergetic Gas Generators, *Advanced Functional Materials*, (03 2013): 0. doi: 10.1002/adfm.201202100
- 11/25/2013 27.00 S. Yan, G. Jian, M.R. ZAchariah. Electrospun NanoFiber Based Thermite Textiles and their Reaction Properties, *ACS Applied Materials and Interfaces*, (04 2012): 6432. doi:
- 11/25/2013 28.00 Nicholas W. Piekiet, , Garth C. Egan, , Kyle T. Sullivan, , Michael R. Zachariah*. Evidence for the Predominance of Condensed Phase Reaction in Chemical Looping Reactions Between Carbon and Oxygen Carriers., *J. Phys. Chem. C*, (10 2012): 244. doi:
- 11/25/2013 29.00 Guoqiang Jian, Snehaunshu Chowdhury, Kyle Sullivan, Michael R. Zachariah. Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition?, *Combustion and Flame*, (02 2013): 0. doi: 10.1016/j.combustflame.2012.09.009
- 11/25/2013 30.00 Haiyang Wang, Guoqiang Jian, Shi Yan, Jeffery B. DeLisio, Chuan Huang, Michael R. Zachariah. Electro spray Formation of Gelled Nano-Aluminum Microspheres with Superior Reactivity, *ACS Applied Materials & Interfaces*, (08 2013): 0. doi: 10.1021/am401238t
- 11/25/2013 32.00 Guoqiang Jian, Karen Gaskell, Aldo Ponce, Panju Shang, Michael R. Zachariah, Daniel A. Kaplowitz. Aerosol Synthesis and Reactivity of Thin Oxide Shell Aluminum Nanoparticles via Fluorocarboxylic Acid Functional Coating, *Particle & Particle Systems Characterization*, (08 2013): 0. doi: 10.1002/ppsc.201300112
- 11/25/2013 34.00 Jingyu Feng, Rohit J. Jacob, Garth C. Egan, Michael R. Zachariah, Guoqiang Jian. Super-reactive Nanoenergetic Gas Generators Based on Periodate Salts, *Angewandte Chemie International Edition*, (09 2013): 0. doi: 10.1002/anie.201303545
- 11/25/2013 35.00 Michael Zachariah. Nanoenergetics: Hype, Reality and Future, , *Propellants, Explosives, Pyrotechnics*, (01 2013): 7. doi:

TOTAL: 24

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
-----------------	--------------

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
-----------------	--------------

10/01/2012 22.00	G. Jian, L. Zhou, N. Piekiet, M.R. Zachariah. Probing Oxygen Release Kinetics of Nanosized Metal Oxides by Temperature-Jump Time of Flight Mass Spectrometry, Eastern Sates Combustion Institute. 09-OCT-11, . . . ,
------------------	--

TOTAL: 1

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
-----------------	--------------

10/01/2012 20.00	G. Feng,, S. Chowdhury, G. Jian,, M.R Zachariah. Modified Aerosol Routes to Core-Shell Nano-Energetic Materials Synthesis, Materials Research Society. 01-DEC-11, . . . ,
------------------	---

TOTAL: 1

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

- 10/01/2012 19.00 K. T. Sullivan,, C. Wu,, N. W. Piekiet, , K. Gaskell, M. R. Zachariah. K. Sullivan, C. Wu. N. Piekiet, K. Gaskell and M.R. Zachariah Synthesis and Reactivity of of Nano-Ag₂O as an Oxidizer in Energetic Systems Yielding Antimicrobial Products, Combustion and Flame (06 2012)
- 10/01/2012 24.00 G. Jian, N. Piekiet, M.R. Zachariah. Time-resolved mass spectrometry of nano-Al and nano-Al/CuO thermite under rapid heating: A mechanistic study, J Phys Chem (07 2011)
- 10/01/2012 21.00 G. Jian, C. Chowdhury, K. Sullivan, M.R. Zachariah. Nanothermite Reactions: Is Gas Phase Oxygen Generation from the Oxygen Carrier an Essential Prerequisite to Ignition?, Combustion and Flame (05 2011)
- 10/01/2012 23.00 G. Jian, L. Liu, M.R. Zachariah. Facile aerosol route to hollow CuO spheres and its superior performance as an oxidizer in nanoenergetic gas-generators, Advanced Functional Materials (05 2012)
- 11/25/2013 33.00 G. Young, , K. Sullivan,, N. Piekiet,, S. Chowdhury, M.R. Zachariah. The Effects of Aluminum Hydride as a Fuel Supplement on the Performance of Traditional NanoThermite, Journal of Propulsion and Power (06 2013)

TOTAL: 5

Number of Manuscripts:

Books

Received

Book

TOTAL:

Received

Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
G. Jian	1.00	
K. Sullivan	0.50	
S. Chowdhury	0.80	
N. Piekiet	0.50	
FTE Equivalent:	2.80	
Total Number:	4	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Michael ZAchariah	0.10	
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

G. Jian

K. Sullivan

S. Chowdhury

N. Piekiet

Total Number:

4

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

"see Attachment"

Technology Transfer

Final Report
Grant # W911NF0610215
Understanding and Quantifying the Reactivity of Energetic NanoParticles and
NanoComposites

M.R. Zachariah
Departments of Mechanical Engineering and Chemistry and Biochemistry
University of Maryland, College Park, MD, 20742

The following report is an executive summary of the project. The details of the project results can be found in the 16 archived publications listed at the end of this document.

Objective: The focus of this work was to understand quantitatively, the nature of the reactivity of nanoparticles and nanocomposites for energetic materials applications. Our approach took two thrusts.

1. Single Particle Kinetics
2. Ensemble Fuel/Oxide Nanocomposite Kinetics.

Our goal was to:

- A. Explore the size resolved reactivity of nanoparticles.
- B. Explain the behavior using phenomenological modeling and compare with bulk materials.
- C. Explore condensed state kinetics using a new type of mass-spectrometry tool.

Approach

- Use novel diagnostic tools to probe reactivity of nanocomposites and tease out mechanisms: Including advanced ion-mobility and mass spectrometry tools.
- Conduct bulk powder measurements in combustion bombs and wires to extract combustion time scales and the role of mixtures and stoichiometry on burning.
- Use new high heating rate electron microscopy to visualize condensed state reactions between nanocomposites.
- Conduct Molecular Dynamics simulations to understand properties of nanoparticles.

Relevance to Army: Energetic materials assembled at the Nanoscale offer the potential to yield more energy over shorter time frame, and thus more power. However critical questions remain as to the actual gains in the temporal energy profile. Furthermore to design materials with enhanced properties a better scientific understanding is needed. The focus of this project was to provide DOD with the critical information needed to assess the utility of nanoenergetic materials to real world application. Additionally we provided DOD with methods for characterizing the reaction kinetics on well controlled and understood reactive metal, oxidizers and their composites.

Significant Accomplishments and Topics Explored:

Studies on the Burning of MIC's

This work investigates the reaction mechanism of Metastable Intermolecular Composites (MICs) by collecting simultaneous pressure and optical signals during combustion in a constant-volume pressure cell. Nanoaluminum and three different oxidizers are studied; CuO, SnO₂, and Fe₂O₃. In addition these mixtures are blended with varying amount of WO₃ as a means to perturb the gas release in the system. The mixtures with CuO and SnO₂ exhibit pressure signals which peak on timescales faster than the optical signal, while the mixtures containing Fe₂O₃ do not show this behavior. The burn time is found to be relatively constant for both CuO and SnO₂, even when a large amount of WO₃ is added. For Fe₂O₃, the burn time decreases as WO₃ is added and the temperature increases. The results are consistent with the idea that oxidizers such as CuO and SnO₂, which decompose at relatively low temperatures, show an initial fast pressure rise followed by combustion over a longer time scale. In this case the burning is rate limited by the aluminum, and is similar to the burning of aluminum in a pressurized oxygenated environment. For the Fe₂O₃ system, the oxidizer decomposition to release oxygen only occurs significantly at the adiabatic flame temperature, and is the rate limiting step.

How is Nano-Aluminum Initiation

One of the questions that has been debated is how the aluminum is initiated. The two primary competing theories have been solid-state diffusion through the oxide shell or the "Melt-Dispersion" mechanism. The latter involves a violent explosion of the oxide shell. To address this point the ignition of nanoscale Al/CuO thermites with different aluminum oxide shell thicknesses was investigated on a fast heated Pt wire. ($\sim 10^5$ K/s). Ramping the wire temperature to ~ 1250 K, and then shutting off the voltage pulse results in ignition well after the pulse it is turned off- ***i.e. an ignition delay is observed***. The delay is used as a probe to extract effective diffusion coefficient of the diffusing species, which is confirmed by fast time- resolved mass spectrometry. The results of this study are consistent with a diffusion controlled ignition mechanism.

Time resolved characterization of Thermite Chemistry/Physics

Heterogeneous nanocomposite reactions of Al/CuO, Al/Fe₂O₃ and Al/ZnO systems were characterized using a recently developed T-Jump/TOF mass spectrometer. Flash-heating experiments with time-resolved mass spectrometry were performed at heating

rates in the range of $\sim 10^5$ K/s. We find that molecular oxygen liberated during reaction is an active ingredient in the reaction. Experiments also conducted for neat Al, CuO, Fe₂O₃ and ZnO powders show that the oxygen are produced by decomposition of oxidizer particles. Mass spectrometric analysis indicates that metal oxide particles behave as an oxygen storage device in the thermite mixture, and release oxygen very fast to initiate the reaction. A clear correlation is observed between the capability of oxygen release from oxidizing particles, and the overall reactivity of the nanocomposite. The high reactivity of Al/CuO mixture can be attributed to the strong oxygen release from CuO, while Fe₂O₃ liberates much less oxygen and leads to moderate reactivity, and ZnO's poor oxygen release capability caused the Al/ZnO mixture to be completely not reacting, even though the reaction is overall exothermic. It is likely that the role of the oxygen species is not only as a strong oxidizer, but also an energy propagation medium that carries heat to neighboring particles.

An experimental investigation on the ignition behavior of γ -Aluminum Hydride (γ -AlH₃) was also conducted. In this study the ignition characteristics were determined through the use of two separate modified T-jump experiments. Both ignition and hydrogen release temperatures were studied for heating rates ranging from 10^4 K/s to 10^5 K/s. Both the hydrogen release and ignition temperature increased as the heating rate increased. Hydrogen release temperatures ranged from approximately 650 K to 1200 K, while ignition was observed to range from below the melting temperature of aluminum (933 K) to approximately 1500 K. Activation energies for hydrogen release were ~ 27 kJ/mol, and are well below those reported by others at much lower heating rates. This result is consistent with the effects of higher heating rates transitioning the rate limiting step from one of chemical kinetics to intra-particle hydrogen diffusion. For conditions in which the particles would ignite it was found that the environment did not play a significant role in the ignition temperature, beyond a critical oxygen mole fraction of $X_{O_2} > 0.05$. Ensemble average burning times were found to increase by a factor of about three when the oxygen mole fraction was increased from 0.1 to 0.5.

Plasma Generation and the Role of Built in E-Fields.

One very interesting observation was that intense ion pulse originate from nanocomposite thermite reactions. We temporally probed them the Temperature Jump/Time of Flight Mass Spectrometer (T-Jump/TOFMS). These ion pulses are observed to be much shorter in duration than the overall thermite reaction time. Ion ejection appears in stages as positive ions are ejected prior to nanocomposite thermite ignition, and ignition of the thermite mixtures leads to a second ionization step which is

primarily dominated by negative species. This observation can be explained by a diffusion based ion-current mechanism, in which strong Al ion diffusion flux formed through the oxide shell, and the surface Na and K ions from salt contaminations are ejected by the strong electrostatic repulsion. The fact that the negative ionization step occurs during the ignition event, suggests a strong relation between the nanocomposite thermite reaction and the negative ionization process.

Using the classical molecular dynamics method we simulate the mechanochemical behavior of small (i.e. core diameter < 10nm) oxide coated aluminum nanoparticles. Aluminum nanoparticles with core diameters of approximately 5nm and 8nm are simulated with 1nm and 2nm thick oxide coatings or shells. In addition to thickness the shells are parameterized by varying degrees of crystallinity, density, and atomic ratios in order to study their affect on the ignition of nanoparticle oxidation. The oxide shells are parameterized to consider oxide coatings with the defects that commonly occur during the formation of an oxide layer and for comparison with a defect free crystalline oxide shell. Computed results include the diffusion coefficients of aluminum cations for each shell configuration and over a range of temperatures. The observed results are discussed and compared with the ignition mechanisms reported in the literature. From this effort we have found that the oxidation ignition mechanism for nanometer sized oxide coated aluminum particles is the result of an enhanced transport due to a built-in electric field induced by the oxide shell. This is in contrast to the currently assumed pressure driven diffusion process. This induced electric field accounts for approximately 90% of the mass flux of aluminum ions through the oxide shell. The computed electric fields show good agreement with published theoretical and experimental results.

Aluminum NanoCrystal Growth

We show a low temperature gas-phase synthesis route to produce faceted aluminum crystals in the aerosol phase. Use of triisobutylaluminum whose decomposition temperature is below the melting point of elemental aluminum enabled us to grow nanocrystals from its vapor. TEM shows both polyhedral crystalline and spherical particle morphologies, but with the addition of an annealing furnace one can significantly enhance production of just the polyhedral particles. The results on surface passivation with oxygen suggest that these nanocrystals are less pyrophoric than the corresponding spherical aluminum nanoparticles, and combustion tests show an increase in energy release compared to commercial nanoaluminum.

On the Role of Reactive Sintering

One of the open questions in understanding the reactivity of nanometric metal/metal oxide composites is the relative role of gas-solid vs. condensed state reactions. We investigated several nano-Al based thermites subjected to very rapid heating rates..

Ignition was seen to occur above the melting temperature of aluminum, and closer to the melting/decomposition temperature of the metal oxide. Samples were also rapidly heated in-situ within electron microscopes to provide direct imaging before and after heating. The sintering of agglomerated particles into larger, spherical particles was experimentally observed in all cases, and the fuel and oxidizer were found to be in surface contact suggesting that condensed-phase reactions had at some point occurred. High resolution image sequences of thermites ignited on the Pt wire were collected using a real time phase contrast imaging technique at the Advanced Photon Source at Argonne National Lab. The timescale of the sintering event was experimentally seen to occur on a faster timescale than the onset of optical emission, suggesting some degree of condensed phase reaction precedes thermal runaway and intense optical emission. The results suggest that a reactive sintering mechanism occurs early in the reaction, causing rapid melting and coalescence of aggregated particles. This dramatically changes the initial size and morphology of the constituents before the remainder of the material burns. The results call into question the idea that a decrease in particle size will necessarily lead to an enhancement in reactivity, since large amounts of sintering occurs early in the reaction.

Microstructural Behavior of the Alumina Shell and Aluminum Core Before and After Melting of Aluminum Nanoparticles

The oxidation mechanisms of nanoaluminum particles, nominally employed as fuel component, is still an unsettled problem, because of the complex nature of the mechanical properties of the oxide shell surrounding the elemental core. Though mechanical breakage of the alumina shell upon or after melting of aluminum core has been thought to play a key role on the combustion of aluminum nanoparticles, there has been little direct evidence. In this study the microstructural behaviors of Al core and alumina shell lattices were investigated with increasing temperatures. Three in situ techniques: high-temperature X-ray diffraction analysis, hot-stage transmission electron microscopy, and high-resolution transmission electron microscopy for heat-treated samples were employed to probe the thermal behaviors of aluminum and alumina lattices before and after melting of the aluminum core. High-temperature X-ray diffraction analysis revealed that nano aluminum lattice was initially expanded under tension at room temperature, and then when heated passes through a zero-strain state at ~ 300 oC. Upon further heating above bulk melting temperature of aluminum, the aluminum lattice expanded under almost no constraint. This interesting observation, that is contrary to almost all of the previous results and models, was ascribed to the inhomogeneous (localized) crystalline phase transformation of amorphous alumina. High-resolution transmission electron microscopy and in situ hot-stage transmission electron microscopy evidenced localized phase transformation accompanied by a

significant shell thickening, presumably resulting from diffusion processes of Al cations and O anions, which is to absorb the pressure built in aluminum core, by creating a more ductile shell.

Nanothermite Reactions: Gas Phase Oxygen Generation from the Oxygen Carrier is not an Essential Prerequisite to Ignition?

In this study we investigate the role of gas phase oxygen on ignition of nanothermite reactions. By separately evaluating the temperature at which ten oxidizers release gas phase species, and the temperature of ignition in an aluminum based thermite, we found that ignition occurred prior to, after or simultaneous to the release of gas phase oxygen depending on the oxidizer. For some nanothermites formulations, we indeed saw a correlation of oxygen release and ignition temperatures. However, when combined with in-situ high heating stage microscopy indicating reaction in the absence of O₂, we conclude that the presence of free molecular oxygen cannot be a prerequisite to initiation for many other nanothermites. This implies that for some systems initiation likely results from direct interfacial contact between fuel and oxidizer, leading to condensed state mobility of reactive species. Initiation of these nanothermite reactions is postulated to occur via reactive sintering, where sintering of the particles can commence at the Tammann temperature which is half the melting temperature of the oxidizers. These results do not imply that gas phase oxygen is unimportant when full combustion commences.

Time-resolved mass spectrometry of nano-Al and nano-Al/CuO thermite under rapid heating: A mechanistic study

Aluminum nanoparticles (Al-NPs) and nano-Al/CuO thermite were investigated in a rapid heating environment by temperature jump time-of-flight mass spectrometry. Upon rapid heating (105 K/s-106 K/s), Al-containing vapor species (Al and Al₂O) are observed to slowly increase with increasing temperature, followed by a rapid increase in concentration at ~2030 K. The temporal evolution of Al, Al₂O species observed in time-resolved mass spectra of rapid heated Al-NPs supports the hypothesis that Al containing species diffuse outwards through the oxide shell under high heating rate conditions. The rapid rise in Al-containing species above 2030 K, which is below the bulk melting point of Al₂O₃ implies that the penetration of Al into the shell probably decreases its melting point. The measurements lead to an effective overall diffusion coefficient ~10⁻¹⁰ cm²/s. Time resolved mass spectra of nano-Al/CuO thermite show for the first time the existence of Al, Al₂O, AlO and Al₂O₂ intermediate reaction

products, with Al₂O₃ the main intermediate oxidation product, in agreement with thermochemical calculations.

Facile aerosol route to hollow CuO spheres and its superior performance as an oxidizer in nanoenergetic gas-generators

Thermochemically metal/metal oxide redox reactions have twice the energy density of TNT. They however suffer from low pressure-volume work due to low gas expansion from the reaction. In this study we focus on developing a nanocomposite that delivers high energy density, and the potential of rapid gas release. Hollow CuO spheres with nanosized building blocks are fabricated using a “droplet-to-particle” aerosol spray pyrolysis method with the introduction of gas blowing agents in the synthesis procedure. Nanoaluminum with hollow CuO as an oxidizer ignites in a very violent manner and exhibits excellent gas generation behavior, demonstrating a high pressurization rate of 0.745 MPa/μs and transient peak pressure of 0.896 MPa with a charge density of 1 mg/cm³, as well as a rapid oxygen release. Compared to the wet chemistry methods, gas-phase processes are relatively low cost, nominally offer a higher purity product, and usually are configured as continuous production processes, with a limited number of steps. The synthesis strategy demonstrated is simple and should be extendable to the preparation of other hollow metal oxide structures.

Decomposition of Aminotetrazole Based Energetic Materials under High Heating Rate Conditions

A T-Jump/Time-of-Flight Mass Spectrometer (T-Jump/TOFMS) is used to probe the decomposition of several aminotetrazole containing energetic materials under very high heating rates of 10⁵-10⁶ K/s. The materials investigated are 5-amino-1-methyl-1H-tetrazolium dinitramide (MeHAT₊DN⁻), 1,5-diamino-4-methyl-1H-tetrazolium dinitramide (MeDAT₊DN⁻), 1,5-diamino-1H-tetrazolium nitrate (DAT₊N⁻), 1,5-diamino-4-methyl-1H-tetrazolium azide (MeDAT₊N₃⁻), and 5-aminotetrazolium dinitramide (HAT₊DN⁻). Subtle differences between materials in functional group placement and anion composition allow for further understanding of the decomposition pathway of the tetrazole structure and various anions. Two decomposition pathways for the tetrazole ring are observed, which result in the primary formation of HN₃ or N₂. The N₂ formation pathway occurs when functional groups are placed symmetrically around the tetrazole ring, while asymmetric placement results in HN₃ production. The differing anion compositions also show effects on thermal stability of the salts as is demonstrated by lower decomposition temperature for the azide containing salt compared to the similar dinitramide containing material. For the decomposition of the dinitramide

molecule, a high temperature (N₂O forming) and low temperature (NO₂ forming) decomposition pathway is observed as has been previously suggested.

Collaborations and Technology Transfer

- Collaboration with Scott Weingarten at ARO on nanostructured Aluminum clusters
- Collaboration with Greg Young at NSWC-IH
- Collaborating with Jason Jouet of NSWC-IH on development of gas phase routes to make surface passivated nanoaluminum.
- Collaboration with Brian Henz at ARL on molecular dynamics simulation of nanoaluminum
- Collaboration with Maggie Hurley at ARL on measurement of decomposition kinetics of high nitrogen energetics
- Collaboration with Greg Young at NSWC-IH on Alane Ignition
- Collaboration with Alex Meissner at NSWC-IH on MD simulation of Nanolaminates
- Collaboration with Luke Currano at ARL on porous silicon based energetics

Resulting Journal Publications

1. L. Zhou, N. Piekiet, S. Chowdhury, D. Lee and M. R. Zachariah *Transient ion emission during nanocomposite thermite reaction* *J. Appl. Phys.* 106, 083306 (2009)
2. G. Young, S. Chowdhury, and M.R. Zachariah *Ignition Behavior of -Alane* *Comb. Sci. Tech.* 182: 1341–1359, 2010
3. K. Sullivan and M.R. Zachariah *Simultaneous Pressure and Optical Measurements of Nanoaluminum Thermite: Investigating the Reaction Mechanism* *Journal of Propulsion and Power*, 26, 467 (2010)
4. B. Henz, T. Hawa, and M.R. Zachariah "On the Role of Built-in Electric Fields on Oxidation of Oxide Coatet NanoAluminum: ion mobility versus Fickian Diffusion" *J. Appl. Phys.* 107, 024901 (2010)
5. S. Chowdhury, K. Sullivan, N. Piekiet, L. Zhou and M. R. Zachariah *Diffusive vs. Explosive Reaction at the Nanoscale* *J. Phys. Chem. C.* 114, 9191 (2010)
6. L. Zhou, N. Piekiet, S. Chowdhury, M.R. Zachariah, "Time Resolved Mass Spectrometry of the Exothermic Reaction between Nanoaluminum and Metal Oxides: The Role of Oxygen Release" *J. Physical Chemistry C.* 114, 14269 (2010)
7. K. Sullivan, C. Johnson, M.R. Zachariah *Ignition and Combustion Characteristics of Nanoscale Al/AgIO₃: A Potential Energetic Biocidal System* *Combustion Science and Technology*, 183, 205 (2011)

8. K. Sullivan, W-C Chiou, R. Fiore and M.R. Zachariah *In-situ microscopy of rapidly heated nano-Al and nano-composite thermites* Appl. Phys. Lett. 97, 133104 (2010)
9. B.J. Henz and M.R. Zachariah "Molecular Dynamic Simulation of Energetic Nanoparticles" Simulation-Based Innovation and Discovery, Chapter 2, Pg 15-45, CECD Series (2011)
10. N. W. Piekiet, R. E. Cavicchi, and M. R. Zachariah *Rapid-Heating of Energetic Materials using a Micro-Differential Scanning Calorimeter* Thermochemica Acta, 521, 125 (2011)
11. D. A. Firmansyah, K. Sullivan, K-S. Lee, Y. H. Kim, R. Zahaf, M. R. Zachariah and D. Lee "Microstructural Behaviors of Alumina Shell and Aluminum Core Before and After Melting of Aluminum Nanoparticles" Journal of Physical Chemistry C. 116, 404 (2012)
12. C. Wu, K. Sullivan,, S. Chowdhury , G. Jian,, L. Zhou, M. R. Zachariah . *Encapsulation of Perchlorate Salts within Metal Oxides for Application as Nano-Energetic Oxidizers*, Advanced Functional Materials, ,(10 2012): 78. doi: 2012/10/01 12 1:477:33
13. N. Piekiet, M.R. Zachariah. N.W. Piekiet and M.R. Zachariah, *Decomposition of Aminotetrazole Based Energetic Materials under High Heating Rate Conditions*, J Phys Chem A, (10 2012): 1519. doi:2012/10/01 12 1:589:51
14. G. Jian, L. Liu and M.R. Zachariah *Facile Aerosol Route to Hollow CuO Spheres and its Superior Performance as an Oxidizer in Nanoenergetic Gas-Generators* Advanced Functional Materials adfm.201202100 (2012)
15. G. Jian, N. Piekiet, and M.R. Zachariah *Time-Resolved Mass Spectrometry of Nano-Al and Nano-Al/CuO Thermite Under Rapid Heating: A Mechanistic Study* J. Phys. Chem. C. 116, 26881 (2012)
16. K. Sullivan, N.W., Piekiet, C. Wu., S. Chowdhury, S.T. Kelley, T.C. Hufnagel, K. Fezzaa, M.R. Zachariah *Reactive Sintering: An Important Component in the Combustion of Nanocomposite Thermites* Combustion and Flame 159, 2 (2012)

Graduate Students supported

- G. Jian-PhD Student
- K. Sullivan – PhD Student
- S. Chowdhury- PhD Student
- N. Piekiet - PhD Student